

Final Report: Summary of Research

Agency: NASA

Award No: NCC2-5516

Project Number: 56000111

Period of Performance: 8/15/02 to 8/14/04

Prepared by:

Grant Smith

Associate Professor

Department of Materials Science and Engineering and

Department of Chemical Engineering

University of Utah

29 December 2004

## Summary of Research

This project has entailed use of molecular simulations to understand complex nanoscale dynamic phenomena in polymer solutions.

### Year 1

The first half of the project concentrated on molecular simulation studies of the translocation of model molecules for single-stranded DNA through a nanosized pore. This has resulted in the publication, **Translocation of a polymer chain across a nanopore: A Brownian dynamics simulation study**, by Pu Tian and Grant D. Smith, JOURNAL OF CHEMICAL PHYSICS VOLUME 119, NUMBER 21 1 DECEMBER 2003, which is attached to this report. In this work we carried out Brownian dynamics simulation studies of the translocation of single polymer chains across a nanosized pore under the driving of an applied field (chemical potential gradient) designed to mimic an electrostatic field. The translocation process can be either dominated by the entropic barrier resulted from restricted motion of flexible polymer chains or by applied forces (or chemical gradient). We focused on the latter case in our studies. Calculation of radius of gyration of the translocating chain at the two opposite sides of the wall shows that the polymer chains are not in equilibrium during the translocation process. Despite this fact, our results show that the one-dimensional diffusion and the nucleation model provide an excellent description of the dependence of average translocation time on the chemical potential gradients, the polymer chain length and the solvent viscosity. In good agreement with experimental results and theoretical predictions, the translocation time distribution of our simple model shows strong non-Gaussian characteristics. It is observed that even for this simple tube-like pore geometry, more than one peak of translocation time distribution can be generated for proper pore diameter and applied field strengths. Both repulsive Weeks–Chandler–Anderson and attractive Lennard-Jones polymer–nanopore interaction were studied. Attraction facilitates the translocation process by shortening the total translocation time and dramatically improve the capturing of polymer chain. The width of the translocation time distribution was found to decrease with increasing temperature, increasing field strength, and decreasing pore diameter.

## Year 2

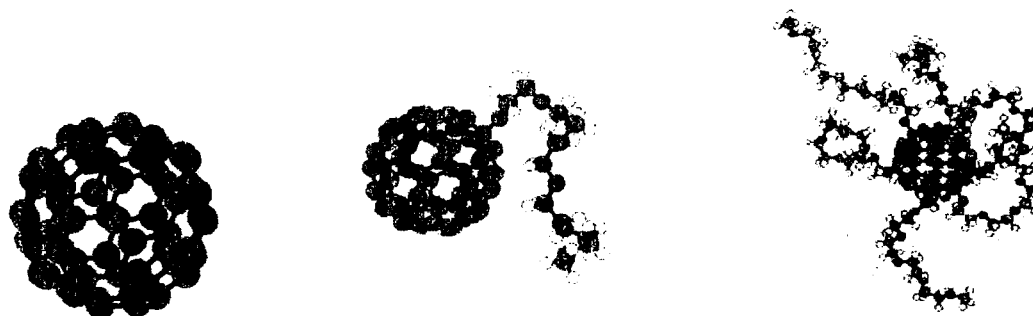


Figure 1.  $C_{60}$  fullerene and PEO modified fullerenes studied.

In the second year of the project we concentrated on the influence of covalently attached water-soluble poly(ethylene oxide) (PEO) chains on the energy dissipation mechanism of  $C_{60}$  fullerenes in aqueous solution. Specifically, we performed molecular dynamics simulations studies of a single  $C_{60}$  fullerene in aqueous solution with no attached PEO chains, a single attached chain, and six attached chains, as shown in Figure 1. In each case, the fullerene was heated to 600 K and the energy of the fullerene, relative to the equilibrium energy at 298 K, was monitored as a function of time, as shown in Figure 2.

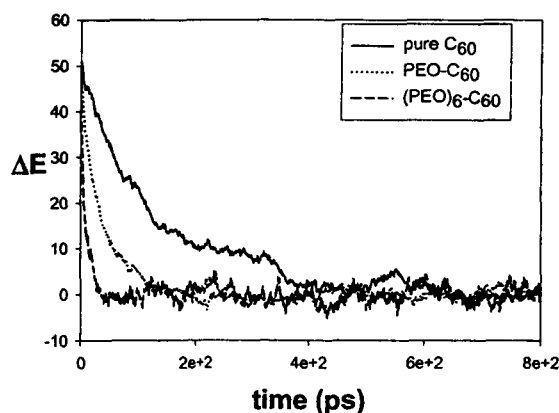


Figure 2. Energy of the fullerene and modified fullerene as a function of time following heating of the fullerene to 600 K.

As can be seen in Figure 2, the rate of energy dissipation is significantly greater for the modified fullerenes, with attachment of a single PEO chain increasing the rate by about one order of magnitude compared to the unmodified fullerene and attachment of six PEO chains increasing the rate by almost two orders of magnitude. In order to better understand why unmodified fullerenes are so inefficient at dissipating thermal energy to

the surround water, and why this efficiency is improved so dramatically with attachment of the water-soluble PEO, we investigated the vibrational spectra the fullerene, the PEO and of water through Fourier transform of the respective velocity autocorrelation functions obtained from molecular dynamics simulations. These spectra are shown in Figure 3.

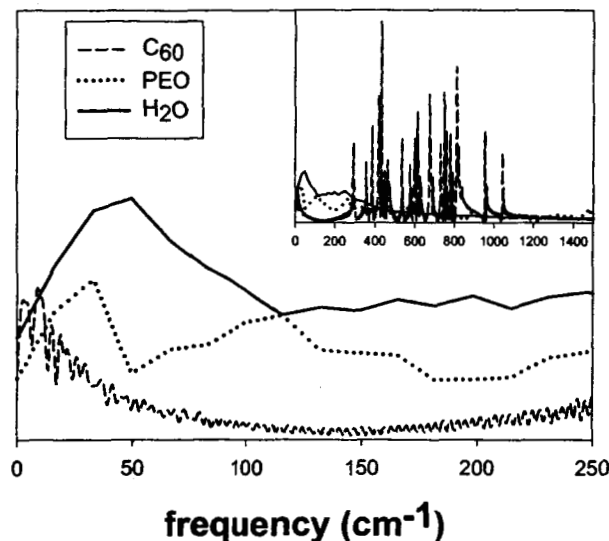


Figure 3. Vibrational spectra of fullerene, PEO and water.

It can be seen that the fullerene has almost no spectral density in frequency range between 50 cm<sup>-1</sup> and 400 cm<sup>-1</sup>, which is the important response range for liquid water. In contrast, PEO does have significant spectral density in this range, and hence can couple thermally with water much more effectively than the fullerene. A manuscript to be submitted to the Journal of Chemical Physics presenting these results is currently in preparation.